# [1,2]-Rearrangement of Imino-*N*-heterocyclic Carbenes − Synthesis and Structures of Chelating Iminoimidazole Pd and Ni Complexes

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**Keywords:** N ligands / Carbenes / Chelates / Transition metals / Rearrangement

Imidazolium and benzimidazolium salts with an *N*-iminoyl and an *N*′-alkyl group are potential precursors for new bidentate [*N*,*C*] ligands which are of interest as novel steering ligands for applications of their metal complexes in homogeneous catalysis. Deprotonation of these azolium salts with potassium hydride does indeed occur, however, the initially formed imino-*N*-heterocyclic carbenes rearrange spontaneously under migration of the *N*-iminoyl group from the nitrogen to the former carbene carbon with the formation of 2-iminoyl(benz)imidazoles. These rearranged compounds are new [*N*,*N*] ligand systems, which can also be synthesized by aluminum-assisted condensation of anilines with the corresponding 2-acylimidazoles. Palladium and nickel [*N*,*N*] complexes have been prepared, characterized by single-crystal X-ray analysis, and briefly evaluated for their catalytic performance in ethylene polymerizations and in Suzuki cross-coupling reactions.



## Introduction

Soon after Arduengo and co-workers[1] isolated the first stable imino-*N*-heterocyclic carbene (NHC) in 1991, the chemistry of these nucleophilic species attracted the interest of many chemists due to their very rich coordination chemistry with almost all elements of the periodic table, and due to the possibility of employing modified and optimized NHC's as steering ligands in metal complexes with catalytic applications, i.e. for carbon-carbon cross-coupling reactions, olefin metathesis, and other reactions.[2] From a historic perspective,[3] metal complexes of simple (in situ generated) NHC's have been studied for over 40 years by the groups of Wanzlick,[4] Lappert,[5] Raubenheimer,[6] Öfele and Herrmann.[2b][2c]

The most common *N*-heterocyclic carbenes are imidazol-2-ylenes containing various *N*-substituents, usually simple alkyl or aryl groups.[2] In recent years tailor-made heterotopic chelating NHCs containing an additional donor functionality gained more and more importance, due to the general focus on applications of NHC metal complexes in catalysis.[2b] Chart 1 gives an overview of selected, recent examples from the current literature[7−9] of [*N*,*C*] and [*C*,*N*,*C*] metal complexes. In addition to the NHC donor, in all reported [*N*,*C*] ligand systems the *N*-donor is part of a planar heterocycle, i.e. pyridine and oxazoline, respectively. To the best of our knowledge, no other *N*-donor functionalities have been investigated as components of heterotopic [*N*,*C*] ligands for potential catalytic applications of their metal complexes, except for one very recent example,[10] published during the preparation of this manuscript.

Conceptually, our motivation for the work reported here is based on the following considerations: We have a general interest in the development of new and improved olefin polymerization catalysts.[11] Up to now, however, there are no NHC metal complexes as olefin polymerization precatalysts, only oligmerization catalysts have been reported.[12] In contrast, ring opening olefin metathesis polymerization (ROMP) is one of the most prominent uses for NHC ruthenium complexes.[13,14] The NHC ligands reported in the literature thus far are not suitable as steering ligands for late transition metal olefin polymerization catalysts based on iron or nickel,[15] because the planar *N*-donor (e.g. pyridine, compare Scheme 1) prevents the axial shielding resulting in suppressed chain termination pathways at the active metal site. The most active non-cyclopentadienyl late transition metal polymerization catalysts are [*N*,*N*,*N*] bis(imino)pyridine iron and [*N*,*N*] bisimine nickel complexes with peripheral sterically demanding *N*-aryl substituents (Scheme 2).[15] We therefore anticipate that [*N*,*C*] and [*N*,*C*,*N*] ligand systems where one *N*-donor is replaced by an NHC moiety will be very promising novel ligands for

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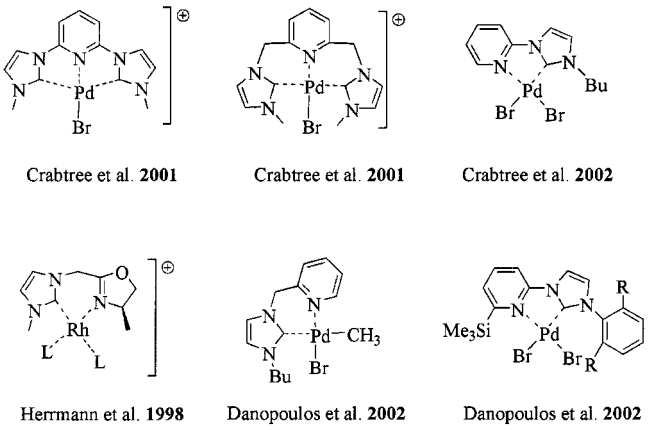
new olefin polymerization precatalysts. In this contribution, we summarize our results on the chemistry of such imino-NHCs and of their metal complexes.

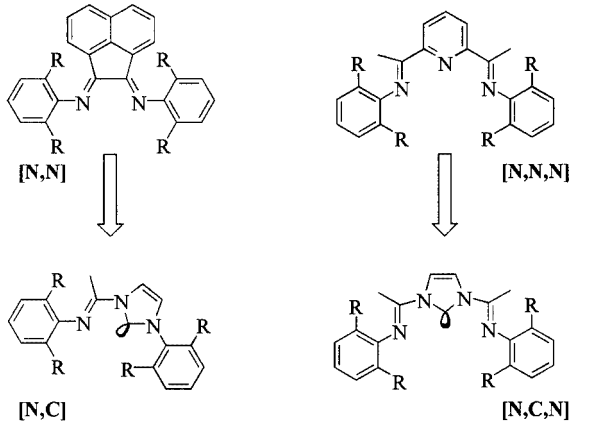



Scheme 1. Recent examples[7−9] of [*N*,*C*] chelating NHC metal complexes

## Results and Discussion

The most versatile and common route to imino-*N*-heterocyclic carbenes consists of deprotonation of their corresponding (benz)imidazolium salts by suitable strong bases.[2] Simple azolium salts are easily accessible by alkylation or arylation of the parent heterocycles, whereas introduction of an additional *N*-donor with sterically demanding substituents is more challenging.

In a first approach, one might assume that condensation of known *N*,*N*′-dibenzoylbenzimidazolium salts[16] with anilines might give access to tridentate [*N*,*C*,*N*] ligand precursors (compare Scheme 2). However, it proved impossible to convert mono- or bis-acylated azolium salts into the corresponding iminoyl derivatives under a variety of experimental conditions. Therefore we chose an alternate synthetic strategy which introduces the imino functionality at an early stage in the synthetic sequence (Scheme 3).




Scheme 2. Design concept for new [*N*,*C*] and [*N*,*C*,*N*] ligands

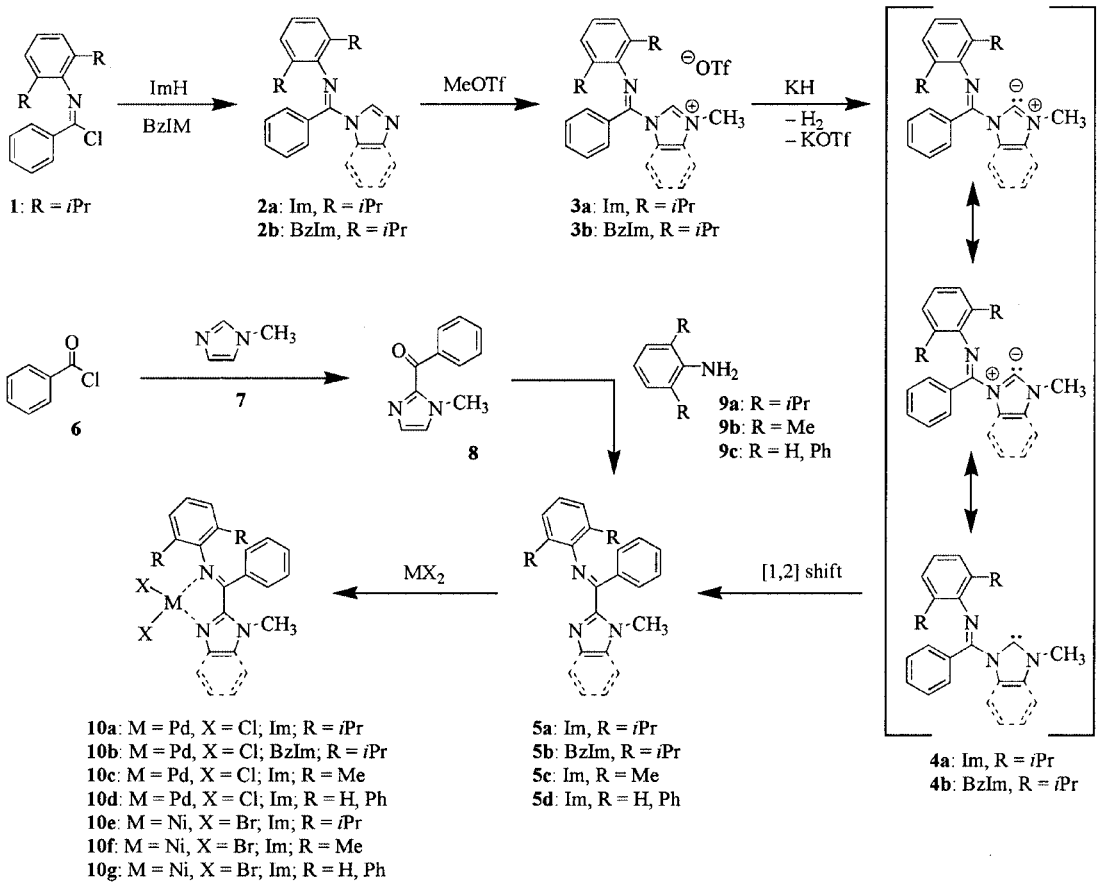
In other work[11b] we found that iminoyl chlorides **1**[17] are very convenient and useful electrophilic reagents which react quantitatively with *N*-H nucleophiles. They also convert imidazole and benzimidazole to the corresponding *N*-iminoyl heterocycles **2a** and **2b** in very good yield. Both compounds are yellow air-stable organic materials with properties in line with their structure (for details see Exp. Sect.). Spectroscopically, the imine group is clearly evident from a strong stretching vibration in the IR spectrum (**2a**: $\nu_{C=N}$ = 1652 cm$^{-1}$; **2b**: $\nu_{C=N}$ = 1651 cm$^{-1}$) and from a low-field $^{13}$C chemical shift of the imine carbon (**2a**: δ = 148.6 ppm; **2b**: δ = 149.9 ppm).

Monoiminoylazoles **2a** and **2b** already contain one sterically bulky *N*-arylated donor − in this case 2,6-diisopropylphenyl − in agreement with the design concept outlined in the introduction. To obtain access to azolium precursors for [*N*,*C*] and [*N*,*C*,*N*] ligands according to Scheme 2, either a simple alkylation step or a second acylation with iminoyl chloride is all that is formally needed.

The attempt at forming *N*,*N*′-bisiminoylazolium salts by reaction of **2a** and **2b** with a second equivalent of iminoyl chloride **1** gave inconclusive results: a reaction did occur but the very air-sensitive product could not be characterized and its follow-up chemistry ruled out the formation of an azolium precursor to a [*N*,*C*,*N*] ligand. After half a year of trying to improve reaction conditions and workup procedures we finally concluded that such tridentate ligand systems are unfortunately not accessible due to fragmentation of the precursor imidazolium species.

On the other hand, the use of azolium salts as the required starting materials for [*N*,*C*] ligands produces no major problems: alkylation at the *N*′-position of **2a** and **2b** is indeed possible using methyl triflate as a highly electrophilic reagent, affording *N*-iminoyl-*N*′-methyl-azolium salts **3a** and **3b**, respectively, in high yield (**3a**: 100%; **3b**: 77%). Other, more common alkylating agents like iodomethane yielded no reaction at all under a variety of experimental conditions, including forced conditions like sealed-tube reactions using excess methyl iodide as solvent and reagent. Both azolium salts are yellow, slightly air-sensitive compounds of surprising stability. Key spectroscopic data include the observation of molecular ions of the cations in the positive mode FAB mass spectra (**3a**: *m*/*z* = 346; **3b**: *m*/*z* = 396), detection of the low-field NMR signal of the azolium hydrogen in the 2-position of the heterocycle [**3a**: δ($^1$H) = 9.09 ppm; **3b**: δ($^1$H) = 9.50 ppm], and observation of the *N*-methyl NMR signals [**3a**: δ($^1$H) = 4.08 ppm, δ($^{13}$C) = 37.6 ppm; **3b**: δ($^1$H) = 4.25 ppm, δ($^{13}$C) = 34.8 ppm]. Interestingly, the $^{13}$C chemical shifts of the imine carbon are almost identical to those of the non-cationic non-methylated starting materials **2a** and **2b** suggesting that the positive charge predominantly located at the *N*-methyl nitrogen. In the case of **3b** suitable crystals for an X-ray structure analysis were obtained (Table 1, Figure 1). In the solid state, the cation of **3b** has a conformation where the imine functionality is oriented away from the 5-ring *N*-heterocycle. Due to steric crowding, the aryl substituents are tilted with respect to the plane of the benzimidazole-imine




Scheme 3. Synthesis of compounds **2**–**10** (ImH = imidazole, BzImH = benzimidazole, *i*Pr = isopropyl, Me = methyl, Ph = phenyl)

moiety by 39.8° (phenyl group) and 76.6° (2,6-diisopropylphenyl group), respectively. The unsymmetric charge distribution indicated by the NMR spectroscopic data in solution is also evident in the crystalline state: The bond length of C(14)–N(2) equals 133.8(4) pm, slightly longer than the value of C(14)–N(3) with 132.0(4) pm, suggesting more double-bond character to this latter bond and more positive charge on the nitrogen N(3) of the *N*-methyl group.

Both azolium salts **3a** and **3b** serve as the key precursors for the corresponding [*N*,*C*] carbenes **4a** and **4b**, respectively (Scheme 3). Reaction of THF solutions of **3a** or **3b** with potassium hydride as base led to the evolution of $H_2$ gas, indicating deprotonation at the imidazole C(2) carbon. Subsequent reaction of these deprotonated (benz)imidazolium species with $PdCl_2$ afforded stable palladium complexes, as anticipated, but their properties and structures (vide infra) were not consistent with [*N*,*C*]$PdCl_2$ complexes. It soon became clear that the initial carbenes **4a** and **4b** must have rearranged by a 1,2-iminoyl shift to C(2)-substituted iminoyl(benz)imidazole **5a** and **5b**, and with "regular" [*N*,*N*] ligands easily formed the [*N*,*N*]$PdCl_2$ complexes **10a** and **10b**, respectively. Low temperature reactions aimed at trapping the initial carbenes **4a** or **4b** failed in all cases, suggesting that this 1,2-rearrangement is an unavoidable process under normal experimental conditions, thereby more or less ruling out the existence of iminocarbenes **4a** and **4b** in the condensed phase. The 1,2-shift of the iminoyl moiety of carbenes **4a** or **4b** is reminiscent of the Stevens rearrangement[18] of acceptor-substituted ammonium salts, but to the best of our knowledge no such migration has ever been described for ylides derived from (benz)imidazolium salts.

In addition we report that the attempted preparation of a Pd complex of **4a** by Raubenheimer's methodology[6] was equally unsuccessful: deprotonation of **2a** followed by complexation with $PdCl_2$ and subsequent methylation with methyl triflate did not afford the desired [*N*,*C*]$PdCl_2$ complex, instead a regular non-chelating imidazole–Pd complex was formed.[19]

The rearrangement of [*N*,*C*] carbenes **4a** and **4b** to [*N*,*N*] ligands **5a** and **5b** prompted us to look for a more versatile synthetic route for this potentially useful ligand framework. To this end, benzoyl chloride **6** was reacted with methylimidazole **7** to afford 2-benzoyl-*N*-methylimidazole (**8**) by a published procedure (Scheme 3).[20] Introduction of the imine functionality was achieved with aluminum-metalated

Table 1. Crystallographic data for **3b**, **10a**, **10b**, **10c**

| Compound | **3b** | **10a** | **10b** | **10c** |
|---|---|---|---|---|
| Molecular formula | $C_{28}H_{30}F_3N_3O_3S$ | $C_{23}H_{27}Cl_2N_3Pd$ | $C_{27}H_{29}Cl_2N_3Pd$ | $C_{19}H_{19}Cl_2N_3Pd$ |
| Molecular mass | 545.61 | 522.78 | 572.83 | 466.67 |
| Crystal system | monoclinic | monoclinic | monoclinic | monoclinic |
| Space group | $P2_1/c$ (No. 14) | $P2_1/c$ (No. 14) | $P2_1/c$ (No. 14) | $P2_1/c$ (No. 14) |
| $a$, pm | 853.60(2) | 1110.34(2) | 1122.59(5) | 1314.09(4) |
| $b$, pm | 2896.60(9) | 1269.48(3) | 1391.70(5) | 966.81(2) |
| $c$, pm | 1185.39(5) | 1649.36(3) | 1622.83(6) | 1518.84(4) |
| α, deg | 90 | 90 | 90 | 90 |
| β, deg | 103.800(2) | 94.566(1) | 91.865(2) | 94.852(1) |
| γ, deg | 90 | 90 | 90 | 90 |
| $Z$ | 4 | 4 | 4 | 4 |
| $V$, nm$^3$ | 2.84632(16) | 2.31748(8) | 2.53402(17) | 1.92273(9) |
| $\rho_{calcd}$, Mg·m$^{-3}$ | 1.273 | 1.498 | 1.502 | 1.612 |
| Temp, K | 233(2) | 233(2) | 293(2) | 233(2) |
| Absorption coefficient (mm$^{-1}$) | 0.166 | 1.045 | 0.963 | 1.249 |
| $F$(000) | 1144 | 1064 | 1168 | 936 |
| Color, habit | colorless prism | orange prism | yellow prism | orange plate |
| Crystal size | 0.3 × 0.2 × 0.12 mm | 0.3 × 0.25 × 0.16 mm | 0.08 × 0.06 × 0.05 mm | 0.35 × 0.3 × 0.15 mm |
| θ range for data collection | 1.90° to 21.00° | 2.03° to 25.00° | 1.93° to 22.00° | 1.97° to 26.00° |
| Index ranges | $0 = h = 8$; $-29 = k = 29$; $-11 = l = 11$ | $0 = h = 13$; $-15 = k = 15$; $-19 = l = 19$ | $0 = h = 11$; $-14 = k = 14$; $-17 = l = 17$ | $0 = h = 16$; $-11 = k = 11$; $-18 = l = 18$ |
| Reflections collected | 11078 | 13548 | 11746 | 11762 |
| Independent reflections | 3042 ($R_{int}$ = 0.0469) | 4070 ($R_{int}$ = 0.0243) | 3107 ($R_{int}$ = 0.0591) | 3768 ($R_{int}$ = 0.0285) |
| Reflections with $I > 2\sigma(I)$ | 2291 | 3631 | 2434 | 3235 |
| Absorption correction | none | none | none | none |
| Refinement method | Full-matrix least-squares on $F^2$ | Full-matrix least-squares on $F^2$ | Full-matrix least-squares on $F^2$ | Full-matrix least-squares on $F^2$ |
| Data/restraints/parameters | 3042/0/345 | 4070/0/264 | 3107/0/300 | 3768/0/231 |
| Goodness-of-fit on $F^2$ | 1.083 | 1.057 | 1.022 | 1.062 |
| Final $R$ int [$I > 2\sigma(I)$] | $R_1$ = 0.0534; $wR_2$ = 0.1406 | $R_1$ = 0.0239; $wR_2$ = 0.0590 | $R_1$ = 0.0348; $wR_2$ = 0.0693 | $R_1$ = 0.0261; $wR_2$ = 0.0627 |
| $R$ int (all data) | $R_1$ = 0.0742; $wR_2$ = 0.1518 | $R_1$ = 0.0291; $wR_2$ = 0.0608 | $R_1$ = 0.0539; $wR_2$ = 0.0745 | $R_1$ = 0.0337; $wR_2$ = 0.0652 |
| Extinction coefficient | 0.0043(10) | 0.0007(2) | 0.00053(19) | 0.0038(3) |
| Largest diff. peak and hole | 343 and −282 e nm$^{-3}$ | 405 and −356 e nm$^{-3}$ | 316 and −260 e nm$^{-3}$ | 367 and −339 e nm$^{-3}$ |

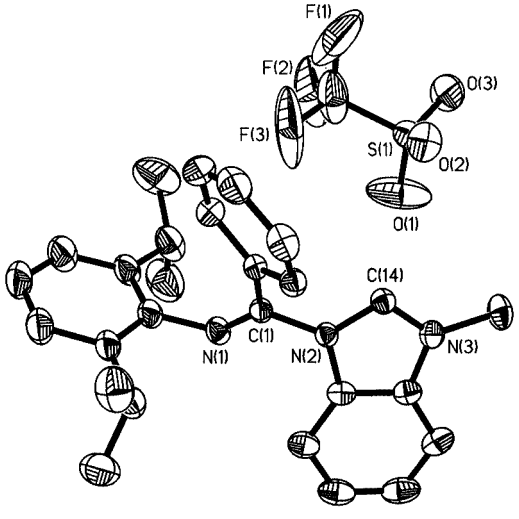



Figure 1. Molecular structure of **3b**; hydrogen atoms are omitted for clarity; selected bond lengths (pm): C(1)−N(1) = 126.1(4), C(1)−N(2) = 145.4(4), N(2)−C(14) = 133.8(4), C(14)−N(3) = 132.0(4); selected angles (°): N(2)−C(14)−N(3) = 110.6(3); tilt angle phenyl group of C(1) versus plane N(1)−C(1)−N(2): 39.8(3); tilt angle 2,6-diisopropylphenyl group of N(1) versus plane N(1)−C(1)−N(2): 76.6(3)

anilines **9a**, **9b**, and **9c** in yields of 68%-85%, thereby allowing steric fine-tuning of these [*N*,*N*] ligand systems. The aluminum-assisted condensation of carbonyl functionalities with primary amines is a very convenient method,[11a,21] which is especially useful for electronically deactivated and sterically crowded systems. Mechanistically it involves a metalation of aniline with trimethylaluminum and sequential formation of the hemiaminal and aminal of the carbonyl moiety, driven by the high oxophilicity of aluminum and by the formation of the thermodynamically very stable Al−O−Al bond of tetramethylaluminoxane.[11a,21] This aluminum-assisted formation of **5a**−**5d** is a necessary synthetic protocol for the chemistry reported in this paper, because standard condensation procedures of **8** with anilines (e.g. acid-catalyzed condensation with aceotropic removal of water) gave only partial conversion into the product in non-useful preparative yields. Compounds **5a**, **5c**, and **5d** are air-stable viscous oils with spectroscopic properties in accordance with their structure (for details see Exp. Sect.). During the course of this work an analogous [*N*,*N*] ligand has been claimed in a patent,[22] although without a phenyl substituent on the imine carbon and without a *N*′-alkyl group. Otherwise the only comparable bidentate *N*-hetero-

cyclic imine ligands reported in the literature are pyridinylimines published three years ago.[23]

Reaction of **5a**, **5c** and **5d** with either $PdCl_2$ or $NiBr_2$ afforded the [*N*,*N*]$MX_2$ complexes **10a**, **10c**−**10g**, respectively, in isolated yields of 65−99% (Scheme 3). Complex **10b** with a benzimidazole backbone has been prepared in 85% yield by the one-pot sequence **3b-4b-5b-10b** (vide supra). All four palladium compounds **10a**−**10d** are orange, air-stable and diamagnetic complexes, indicating the expected regular square-planar coordination geometry at the palladium center. In contrast, all three nickel complexes **10e**−**10f** are green-brown, highly air-sensitive and strongly paramagnetic compounds, suggesting a tetracoordinate tetrahedrally distorted geometry in the case of monomeric complexes, or a bromine-bridged pentacoordinate coordination sphere in the case of dimeric complexes. The paramagnetism of these nickel compounds prevented NMR spectroscopic characterization, on the other hand it is clear evidence for the "designed" steric bulk of the [*N*,*N*] ligands **5a**, **5c** and **5d**.

The different substitution patterns of the *N*-aryl groups of palladium complexes **10a**−**10d** is obviously responsible for varying solubility in this series of complexes: compounds **10a** and **10c** are soluble in common organic solvents, allowing their routine characterization by NMR spectroscopic analysis, but complexes **10b** and **10d** showed only insufficient solubilities even in polar solvents like acetonitrile, acetone and dimethyl sulfoxide, preventing detection of their NMR signals. For compounds **10a** and **10c** the $^{13}C$ signal of the imine carbon (**10a**: $\delta_{C=N}$ = 165.7 ppm; **10c**: $\delta_{C=N}$ = 167.5 ppm) is shifted to lower field by approximately 7 ppm in comparison with the non-complexed free ligands **5a** and **5c**.

Single crystals for X-ray analyses were obtained for complexes **10a**−**10c** (Table 1, Figures 2−4). Overall, all three compounds show the expected square-planar coordination geometry at the palladium centers, deviations from the ideal 90° angle are most pronounced for the structurally enforced [*N*,*N*] chelate (angle N−Pd−N; **10a**: 79.7°, **10b**: 79.8°, **10c**: 79.6°) whereas all other angles are, more or less, close to the ideal value (**10a**: 91.3°-97.4°, **10b**: 89.1°-95.8°, **10c**: 92.2°-95.7°). On the other hand, due to steric crowding, the phenyl groups and the peripheral *N*-aryl groups show large tilt angles of 71.9° to 87.4° in relation to the coordination plane. Clearly visible in Figures 2−4 is the different steric shielding of the palladium metal centers by the differently substituted *N*-aryl groups, indicating "steric control" in these precatalysts by employment of different building blocks. The lengths of the Pd−Cl bonds (226.9−228.4 pm) and of the Pd−N bonds (199.1−207.8 pm) are unexceptional. The bond lengths of the coordinated imine moieties are distinctly shorter (129.7−130.3 pm) in comparison with those of the coordinated N=C double bonds (132.7−133.4 pm) of the (benz)imidazole rings.

Some preliminary catalytic screenings were performed with these new palladium and nickel precatalysts. Ethylene polymerization experiments with methylaluminoxane (MAO) activated nickel complexes **10e**−**10g** in homogeneous solution (70 °C, 20 bar ethylene pressure) showed only very low activities, indicating the predominance of chain termination processes. This result is not too unexpected, because axial shielding of the active metal site in these nickel complexes is insufficient due to the sterically "open"

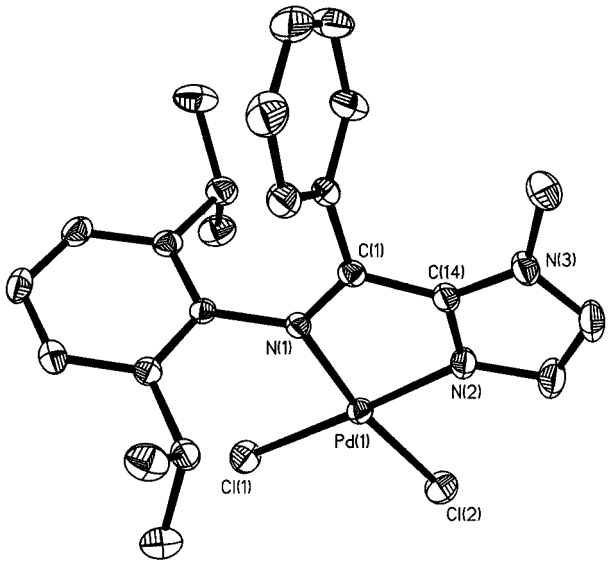



Figure 2. Molecular structure of **10a**; hydrogen atoms are omitted for clarity; selected bond lengths (pm): Pd(1)−Cl(1) = 228.36(6), Pd(1)−Cl(2) = 228.15(6), Pd(1)−N(1) = 207.75(17), Pd(1)−N(2) = 199.20(19), C(1)−N(1) = 130.3(3), C(1)−C(14) = 145.4(3), N(2)−C(14) = 132.7(3), C(14)−N(3) = 136.1(3); selected angles (°): Cl(1)−Pd(1)−Cl(2) = 91.60(2); Cl(1)−Pd(1)−N(1) = 97.40(5); Cl(2)−Pd(1)−N(2) = 91.25(6); N(1)−Pd(1)−N(2) = 79.73(7); N(1)−C(1)−C(14) = 113.86(19); N(2)−C(14)−C(1) = 118.23(19); tilt angle phenyl group of C(1) versus plane N(1)−C(1)−C(14): 71.9(1); tilt angle 2,6-diisopropylphenyl group of N(1) versus plane N(1)−C(1)−C(14): 74.9(2)

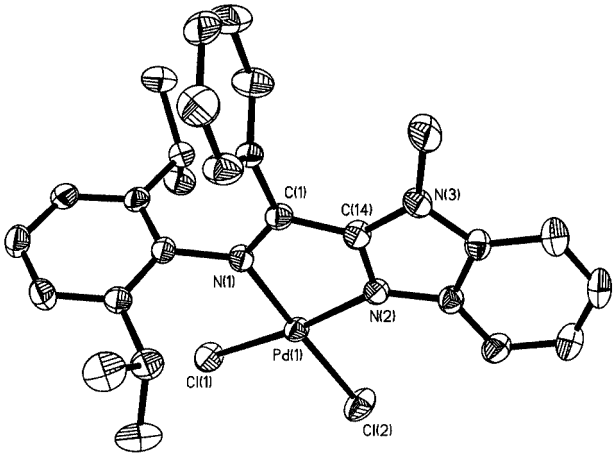



Figure 3. Molecular structure of **10b**; hydrogen atoms are omitted for clarity; selected bond lengths (pm): Pd(1)−Cl(1) = 227.93(12), Pd(1)−Cl(2) = 226.91(13), Pd(1)−N(1) = 204.4(3), Pd(1)−N(2) = 202.6(3), C(1)−N(1) = 129.7(5), C(1)−C(14) = 147.0(6), N(2)−C(14) = 133.1(5), C(14)−N(3) = 136.7(5); selected angles (°): Cl(1)−Pd(1)−Cl(2) = 89.10(5); Cl(1)−Pd(1)−N(1) = 95.52(10); Cl(2)−Pd(1)−N(2) = 95.79(11); N(1)−Pd(1)−N(2) = 79.77(14); N(1)−C(1)−C(14) = 113.8(4); N(2)−C(14)−C(1) = 117.6(4); tilt angle phenyl group of C(1) versus plane N(1)−C(1)−C(14): 86.2(2); tilt angle 2,6-diisopropylphenyl group of N(1) versus plane N(1)−C(1)−C(14): 79.5(3)

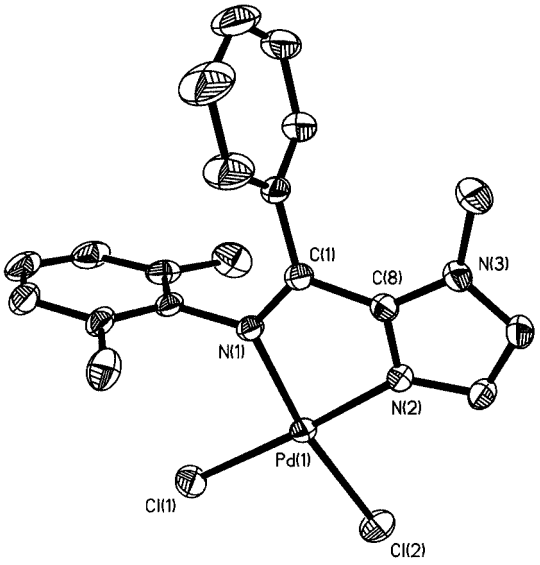



Figure 4. Molecular structure of **10c**; hydrogen atoms are omitted for clarity; selected bond lengths (pm): Pd(1)−Cl(1) = 228.11(7), Pd(1)−Cl(2) = 227.73(7), Pd(1)−N(1) = 205.7(19), Pd(1)−N(2) = 199.1(2), C(1)−N(1) = 130.2(3), C(1)−C(8) = 146.0(3), N(2)−C(8) = 133.4(3), C(8)−N(3) = 135.1(3); selected angles (°): Cl(1)−Pd(1)−Cl(2) = 92.76(3); Cl(1)−Pd(1)−N(1) = 95.65(5); Cl(2)−Pd(1)−N(2) = 92.16(6); N(1)−Pd(1)−N(2) = 79.60(7); N(1)−C(1)−C(8) = 113.1(2); N(2)−C(8)−C(1) = 117.5(2); tilt angle phenyl group of C(1) versus plane N(1)−C(1)−C(8): 76.6(2); tilt angle 2,6-dimethylphenyl group of N(1) versus plane N(1)−C(1)−C(8): 87.4(2)

imidazole side of the bidentate iminoylimidazole ligands. On the other hand, palladium complexes **10a**, **10c**, **10d** are efficient catalysts for Suzuki carbon-carbon cross-coupling reactions: aromatic boronic acids are quantitatively coupled with aryl bromides without formation of undesired homo-coupled products. However, only bromo electrophiles are sufficiently activated for this reaction, attempts to cross-couple boronic acids with the industrially more important chloro aromatics gave no conversion at all.

## Conclusion

The work reported in this contribution is motivated by the search for novel bidentate [*N*,*C*] ligand systems as steering ligands for late transition metal complexes with applications in polymerization catalysis and fine chemical synthesis. Conceptually, the new ligands should contain one imine donor with a sterically demanding *N*-aryl substituent and a *N*-heterocyclic carbene (NHC) as the second donor site. Synthetically, imidazole and benzimidazole are *N*-derivatized with iminoyl chloride followed by *N′*-alkylation with methyl triflate, affording novel iminoyl(benz)imidazolium salts of surprising stability. An X-ray structure and NMR spectroscopic data of benzimidazolium triflate indicate that the positive charge resides predominantly at the *N′*-methyl side, suggesting that the *N*-iminoyl moiety is in a "normal" chemical environment, thereby explaining the unusual stability of this azolium salt. Deprotonation of these (benz)imidazolium triflates at the (benz)imidazole C(2) carbon using potassium hydride as base is successful, however, the initially formed imino-NHC rearranges by a Stevens 1,2-shift to 2-iminoyl(benz)imidazoles which are new [*N*,*N*] ligand systems. These are also synthesized by an alternate synthetic route, which introduces the *N*-aryl group by an aluminum-assisted condensation of anilines with 2-benzoyl-1-methylimidazole. The [*N*,*N*] palladium complexes derived from these ligands are regular square-planar, diamagnetic complexes, as shown by single-crystal structure analysis of three representatives. In contrast, the [*N*,*N*] nickel complexes are highly air-sensitive and strongly paramagnetic complexes, due to ligand induced distortions. Preliminary catalytic tests of olefin polymerizations and of C−C cross-coupling reactions are performed, showing that the palladium complexes are useful catalysts for Suzuki reactions, but the nickel complexes are only poor catalysts for MAO-cocatalyzed ethylene polymerizations.

## Experimental Section

**General:** Commercially available starting materials were used as obtained. Solvents were dried, deoxygenated and saturated with argon according to standard procedures in organometallic chemistry. Reactions of air-sensitive materials were performed in Schlenk glassware in an atmosphere of argon by techniques common in inorganic/organometallic chemistry. New compounds were characterized by MS and IR and NMR spectroscopy, etc by current state of the art procedures, details of instrumentation have been published previously.[24]

**Imidazole 2a:** A Schlenk tube was charged with imidazole (1.76 g, 25.8 mmol) and dry dichloromethane (40 mL). *N*-(2,6-diisopropylphenyl)benziminoyl chloride[11b,16] **1** (12.3 mmol) dissolved in dichloromethane (30 mL) was added to this solution. Imidazolium chloride immediately precipitated, indicating fast formation of the product. Stirring at ambient temperature was continued for 3 hours. Workup: 150 mL of water was added to the mixture to dissolve and remove the imidazolium chloride, the organic product was extracted with three portions of dichloromethane, the combined organic layers were washed with a brine solution, the dichloromethane solution of the product was dried with $Na_2SO_4$ and concentrated in vacuo to a volume of approximately 5 mL. After an equal volume of *n*-hexane was added, 3.30 g **2a** crystallized in the form of a yellow, microcrystalline solid in 81% yield, m.p: 112−115 °C. IR (KBr): $\tilde{\nu}$ = 2969 (w), 2962 (m), 1652 (s), 1602 (w), 1590 (m), 1515 (m), 1469 (s), 1439 (s), 1376 (s), 1364 (m), 1333 (m), 1314 (s), 1297 (s), 1283 (m), 1239 (s), 1160 (s), 1059 (s), 1023 (s), 940 (m), 918 (s), 835 (s), 706 (s), 700 (s) $cm^{-1}$. MS (FAB): *m*/*z* = 331 $[M]^+$. $^1H$ NMR (300 MHz, $CDCl_3$): δ = 0.89 [d, $^3J_{H,H}$ = 6.6 Hz, 6 H, $CH(CH_3)_2$], 1.07 [d, $^3J_{H,H}$ = 6.6 Hz, 6 H, $CH(CH_3)_2$], 2.82 [2 H, sept., 2 × $CH(CH_3)_2$], 6.65−7.71 (m, 10 H, $C_6H_5$, $C_6H_3$, $C_3H_3N_2$), 7.91 (s, 1 H, $C_3H_3N_2$) ppm. $^{13}C$ NMR (75.432 MHz, $CDCl_3$): δ = 21.7, 23.8, 28.4 [$CH(CH_3)_2$], 118.0, 122.8, 124.1, 128.3, 128.9, 129.9, 130.2, 130.7, 136.6, 137.3, 141.9 ($C_6H_5$, $C_6H_3$, $C_3H_3N_2$), 148.6 (C=N) ppm. $C_{22}H_{25}N_3$ (331.46): calcd. C 79.72, H 7.60, N 12.68; found C 80.00, H 7.63, N 12.63.

**Benzimidazole 2b:** A Schlenk tube was charged with benzimidazole (761 mg, 6.44 mmol) and dry dichloromethane (70 mL). *N*-(2,6-diisopropylphenyl)benziminoyl chloride[11b,17] **1** (3.07 mmol) dissolved in dichloromethane (8 mL) was added to this solution.

Benzimidazolium chloride immediately precipitated, indicating fast formation of the product. Stirring at ambient temperature was continued for 4 hours. Workup: 150 mL of water was added to the mixture to dissolve and remove the benzimidazolium chloride, the organic product was extracted with three portions of dichloromethane, the combined organic layers were washed with a brine solution, the dichloromethane solution of the product was dried with $Na_2SO_4$ and concentrated in vacuo to a volume of approximately 5 mL. After an equal volume of *n*-hexane was added, 1.12 g **2b** crystallized in the form of a yellow, microcrystalline solid in 96% yield. m.p.: 123−127 °C. IR (KBr): $\tilde{\nu}$ = 2963 (w), 2867 (m), 1651 (s), 1609 (s), 1588 (s), 1493 (s), 1451 (s), 1369 (s), 1290 (m), 1217 (s), 1161 (m), 1057 (m), 931 (s), 800 (s), 764 (s), 708 (s), 698 (s) $cm^{-1}$. MS (FAB): *m*/*z* = 381 $[M]^+$. $^1H$ NMR (300 MHz, $CDCl_3$): δ = 0.95−1.27 [m, 12 H, $CH(CH_3)_2$], 2.92−3.19 [m, 2 H, 2 × $CH(CH_3)_2$], 7.02−8.07 (m, 12 H, $C_6H_5$, $C_6H_3$, $C_7H_5N_2$) ppm. $^{13}C$ NMR (75.432 MHz, $CDCl_3$): δ = 21.8, 24.2, 28.4, 28.8 $[CH(CH_3)_2]$, 115.3, 120.4, 122.9, 123.5, 124.0, 124.7, 127.2, 128.6, 128.9, 130.8, 131.7, 136.7, 142.2, 143.0, 146.4 ($C_6H_5$, $C_6H_3$, $C_7H_5N_2$), 149.9 (C=N) ppm. $C_{26}H_{27}N_3$ (381.52): calcd. C 81.85, H 7.13, N 11.01; found C 81.98, H 7.15, N 10.97.

**Imidazolium Triflate 3a:** A Schlenk tube was charged with **2a** (150 mg, 0.453 mmol) and dry dichloromethane (40 mL). The solution was cooled to −80 °C and methyltrifluoromethansulfonate (50 µL, 0.453 mmol) was added via a syringe. After 20 minutes stirring at −80 °C, the cooling bath was removed and the mixture was stirred for a further 2 hours, resulting in a clear bright yellow solution. Thin layer chromatography (TLC) indicated complete reaction, all starting material had been consumed with the formation of a polar non-eluting product. Workup: all volatile materials were removed on a vacuum line, the solid yellow residue was washed with two portions of dry diethyl ether and dried in vacuo, affording 224 mg **3a** as a yellow, moderately air-sensitive powder in 100% yield. MS (FAB): *m*/*z* = 346 [M of cation]$^+$. $^1H$ NMR (300 MHz, $CD_2Cl_2$): δ = 0.93 (d, $^3J_{H,H}$ = 6.9 Hz, 6 H, $CH(CH_3)_2$], 1.12 [d, $^3J_{H,H}$ = 6.6 Hz, 6 H, $CH(CH_3)_2$], 2.81 (m, 2 H, 2 × $CH(CH_3)_2$], 4.08 (s, 3 H, $CH_3$), 7.07−7.87 (m, 10 H, $C_6H_5$, $C_6H_3$, $C_3H_3N_2$), 9.09 (s, 1 H, $C_3H_3N_2$) ppm. $^{13}C$ NMR (75.432 MHz, $CD_2Cl_2$): δ = 21.9, 24.1, 28.8 $[CH(CH_3)_2]$, 37.6 (N−$CH_3$), 118.9, 120.5, 123.7, 124.9, 125.8, 129.4, 129.5, 132.7, 136.9, 137.0, 140.8 ($C_6H_5$, $C_6H_3$, $C_3H_3N_2$), 147.3 (C=N) ppm. $C_{24}H_{28}F_3N_3O_3S$ (495.56): calcd. C 58.17, H 5.70, N 8.48; found C 58.08, H 5.72, N 8.43.

**Benzimidazolium Triflate 3b:** A Schlenk tube was charged with **2b** (214 mg, 0.561 mmol) and dry dichloromethane (40 mL). The solution was cooled to −80 °C and methyltrifluoromethansulfonate (62 µL, 0.561 mmol) was added via a syringe. After 20 minutes stirring at −80 °C, the cooling bath was removed and the mixture was stirred for a further 2 hours, resulting in a clear bright yellow solution. Thin layer chromatography (TLC) indicated complete reaction, all starting material had been consumed with the formation of a polar non-eluting product. Workup: all volatile materials were removed on a vacuum line, the solid yellow residue was washed with two portions of dry diethyl ether and dried in vacuo, affording 236 mg **3b** as a yellow, moderately air-sensitive powder in 77% yield. MS (FAB): *m*/*z* = 396 [M of cation]$^+$. $^1H$ NMR (300 MHz, $CD_2Cl_2$): δ = 0.95 (d, $^3J_{H,H}$ = 6.9 Hz, 6 H, $CH(CH_3)_2$], 1.14 [d, $^3J_{H,H}$ = 6.6 Hz, 6 H, $CH(CH_3)_2$], 2.92 [m, 2 H, 2 × $CH(CH_3)_2$], 4.25 (s, 3 H, $CH_3$), 7.11−8.09 (m, 12 H, $C_6H_5$, $C_6H_3$, $C_7H_5N_2$), 9.50 (s, 1 H, $C_7H_5N_2$) ppm. $^{13}C$ NMR (75.432 MHz, $CD_2Cl_2$): δ = 21.9, 24.4, 28.8 $[CH(CH_3)_2]$, 34.8 (N−$CH_3$), 113.7, 117.4, 123.7, 125.8, 128.5, 128.9, 129.6, 129.7, 130.7, 132.7, 136.9, 141.1, 143.2 ($C_6H_5$, $C_6H_3$, $C_3H_3N_2$), 149.1 (C=N) ppm. $C_{28}H_{30}F_3N_3O_3S$ (545.62): calcd. C 61.64, H 5.54, N 7.70; found C 61.53, H 5.57, N 7.66. Single crystal X-ray structure: Table 1, Figure 1.

**Ketone 8:**[20] A round-bottom flask was charged (without protection from air) with 1-methylimidazole **7** (10 mL, 0.125 mol) and acetonitrile (125 mL). The stirred solution was cooled to 0 °C and benzoyl chloride **6** (14.6 mL) was added from a dropping funnel within a period of 15 minutes, followed by addition of triethylamine (17.5 mL, 0.125 mol). The mixture was stirred overnight at ambient temperature, resulting in a yellow solution and a white precipitate of triethylammonium chloride. The ammonium salt was filtered off, solvents and other volatile materials were removed on a rotary evaporator, affording crude **8** as a yellow oil. Distillation in an oil pump vacuum gave 17.5 g (75%) pure **8** as a yellow viscous liquid, b.p. 120−125 °C. MS (EI): *m*/*z* = 186 $[M]^+$. $^1H$ NMR (300 MHz, $CD_2Cl_2$): δ = 4.03 (s, 3 H, $CH_3$), 7.13−7.18 (d, 2 H, $C_3H_2N_2$), 7.45−7.58 (m, 3 H, $C_6H_5$), 8.26−8.29 (d, 2 H, $C_6H_5$) ppm. $^{13}C$ NMR (75.432 MHz, $CD_2Cl_2$): δ = 36.6 (N−$CH_3$), 127.3, 128.2, 129.3, 131.1, 132.8, 137.8, 143.5 ($C_6H_5$, $C_3H_2N_2$), 184.1 (C=O) ppm. $^1H$ NMR spectroscopic data and the boiling point concur with published data.[20]

**Imidazole 5a:** A Schlenk tube was charged with 2,6-diisopropylaniline **9a** (2 mL, 10.6 mmol), toluene (40 mL), and 5.3 mL of a 2.0 molar toluene solution of trimethylaluminum (10.6 mmol). The stirred solution was heated to 80 °C. After 90 minutes methane evolution was completed and the solution was cooled to ambient temperature. Under protection from air, (1-methyl-2-imidazolyl)-phenylketone (**8**) (986 mg, 5.30 mmol) was added in one portion, and an immediate color change from yellow to burgundy red was observed. The mixture was stirred overnight at ambient temperature and heated to 80 °C for a further three hours, affording a bright yellow solution. Workup: the solution was cooled to 0 °C, the mixture was carefully hydrolyzed with crushed ice, the organic product was extracted with three portions of diethyl ether, the combined organic layers were washed with one portion of a 5% aqueous NaOH solution, the diethyl ether solution was washed with two portions of water, the organic phase was dried with $Na_2SO_4$, and all volatile materials were removed in vacuo on a rotary evaporator, affording the crude product together with 2,6-diisopropylaniline. Chromatography on alumina with diethyl ether/*n*-hexane (v/v, 1:1) as eluent afforded 1.45 g pure **5a** in 79% yield as a yellow oil. MS (EI): *m*/*z* = 345 $[M]^+$. $^1H$ NMR (300 MHz, $CDCl_3$): δ = 0.89 [d, $^3J_{H,H}$ = 6.9 Hz, 6 H, $CH(CH_3)_2$], 1.10 [d, $^3J_{H,H}$ = 6.6 Hz, 6 H, $CH(CH_3)_2$], 2.87 [m, 2 H, 2 × $CH(CH_3)_2$], 4.08 (s, 3 H, N−$CH_3$), 6.98−7.17 (m, 10 H, $C_6H_5$, $C_6H_3$, $C_3H_2N_2$) ppm. $^{13}C$ NMR (75.432 MHz, $CDCl_3$): δ = 21.6, 24.3, 28.2 $[CH(CH_3)_2]$, 36.8 (N−$CH_3$), 122.6, 123.5, 125.4, 127.3, 128.4, 129.0, 129.2, 134.8, 135.5, 144.6, 144.9 ($C_6H_5$, $C_6H_3$, $C_3H_2N_2$), 158.5 (C=N) ppm. $C_{23}H_{27}N_3$ (345.49): calcd. C 79.96, H 7.88, N 12.16; found C 80.05, H 7.86, N 12.12.

**Imidazole 5c:** A Schlenk tube was charged with 2,6-dimethylaniline (**9b**) (2.5 mL, 20.3 mmol), toluene (40 mL) and 10.2 mL of a 2.0 molar toluene solution of trimethylaluminum (20.3 mmol). The stirred solution was heated to 80 °C. After 90 minutes methane evolution was completed and the solution was cooled to ambient temperature. Under protection from air, (1-methyl-2-imidazolyl)-phenylketone (**8**) (1.89 g, 10.2 mmol) was added in one portion, and an immediate color change from yellow to burgundy red was observed. The mixture was stirred over the weekend at ambient temperature, affording a bright yellow solution. Workup: the solution was cooled to 0 °C, the mixture was carefully hydrolyzed with crushed ice, the organic product was extracted with three portions of diethyl ether, the combined organic layers were washed with one

portion of a 5% aqueous NaOH solution, the diethyl ether solution was washed with two portions of water, the organic phase was dried with $Na_2SO_4$, and all volatile materials were removed in vacuo on a rotary evaporator, affording the crude product together with 2,6-dimethylaniline. Chromatography on alumina with diethyl ether/*n*-hexane (v/v, 1:1) as eluent afforded 2.0 g pure **5c** in 68% yield as a yellow oil. MS (EI): $m/z$ = 289 $[M]^+$. $^1H$ NMR (300 MHz, $CD_2Cl_2$): δ = 2.09 (s, 6 H, $CH_3$), 4.15 (s, 3 H, N−$CH_3$), 6.82−7.24 (m, 10 H, $C_6H_5$, $C_6H_3$, $C_3H_2N_2$) ppm. $^{13}C$ NMR (75.432 MHz, $CD_2Cl_2$): δ = 18.8 ($CH_3$), 37.6 (N−$CH_3$), 123.2, 125.9, 126.1, 127.6, 127.9, 128.5, 128.9, 129.3, 136.7, 144.8, 148.4 ($C_6H_5$, $C_6H_3$, $C_3H_2N_2$), 159.8 (C=N) ppm. $C_{19}H_{19}N_3$ (289.38): calcd. C 78.86, H 6.62, N 14.52; found C 78.99, H 6.62, N 14.48.

**Imidazole 5d:** A Schlenk tube was charged with 2-aminobiphenyl (**9c**) (1.9 g, 11.2 mmol), toluene (40 mL), and 5.6 mL of a 2.0 molar toluene solution of trimethylaluminum (11.2 mmol). The stirred solution was heated to 80 °C. After 90 minutes methane evolution was completed and the solution was cooled to ambient temperature. Under protection from air, (1-methyl-2-imidazolyl)phenylketone (**8**) (1.05 g, 5.61 mmol) was added in one portion, and an immediate color change from yellow to burgundy red was observed. The mixture was stirred for 48 hours at ambient temperature, affording a bright yellow solution. Workup: the solution was cooled to 0 °C, the mixture was carefully hydrolyzed with crushed ice, the organic product was extracted with three portions of diethyl ether, the combined organic layers were washed with one portion of a 5% aqueous NaOH solution, the ether solution was washed with two portions of water, the organic phase was dried with $Na_2SO_4$, and all volatile materials were removed in vacuo on a rotary evaporator, affording the crude product together with 2-aminobiphenyl. Chromatography on alumina with diethyl ether/*n*-hexane (v/v, 1:1) as eluent afforded 1.61 g pure **5d** in 85% yield as a yellow oil. MS (EI): $m/z$ = 337 $[M]^+$. $^1H$ NMR (300 MHz, $CDCl_3$): δ = 2.69, 4.15 (s, 3 H, N−$CH_3$, *E*/*Z* isomers in 1:2 ratio), 6.59−7.72 (m, 16 H, $C_6H_5$, $C_{12}H_9$, $C_3H_2N_2$) ppm. $^{13}C$ NMR (75.432 MHz, $CDCl_3$): δ = 33.3, 37.2 (N−$CH_3$, *E*/*Z* isomers in 1:2 ratio), 120.8, 121.2, 124.2, 125.1, 125.9, 127.0, 127.8, 128.2, 128.8, 128.9, 129.2, 129.4, 129.6, 129.8, 130.4, 131.4, 132.9, 133.5, 135.4, 138.3, 140.1, 140.4, 142.2, 144.8, 147.7, 148.2, 158.3 ($C_6H_5$, $C_{10}H_9$, $C_3H_2N_2$), 160.2 (C=N) ppm. $C_{23}H_{19}N_3$ (337.42): calcd. C 81.87, H 5.68, N 12.45; found C 81.96, H 5.71, N 12.39.

**Palladium(II) Complex 10a**. **Method A:** A Schlenk tube was charged with **3a** (145 mg, 0.293 mmol), THF (40 mL), and an excess of potassium hydride (25 mg, 0.62 mmol). $H_2$ evolution commenced immediately and the mixture was stirred for 3 hours at ambient temperature, after this time no more gas evolution was observed. The slightly yellow suspension was filtered under protection from air through a short plug of glass wool to remove excess KH and most of the potassium trifluoromethanesulfonate. Palladium dichloride (52 mg, 0.293 mmol) was added to the resulting slightly turbid solution and the mixture was stirred at room temperature for 20 hours, resulting in a brown suspension. Workup: the volatiles were removed on a rotary evaporator, the brown residue was chromatographed on alumina with dichloromethane and acetonitrile as eluent, the brown fraction was decolorized with activated charcoal, and the solvents were removed in vacuo, affording 100 mg of **10a** as a tan solid in 65% yield.

**Method B:** A Schlenk tube was charged with **5a** (630 mg, 1.82 mmol), acetonitrile (30 mL) and $PdCl_2$ (323 mg, 1.82 mmol). The mixture was stirred overnight at ambient temperature to afford an orange solution. Workup: the solution was filtered through celite and chromatographed on silica with dichloromethane and acetonitrile as eluent, the orange fraction was collected, solvents were removed on a rotary evaporator, and the product was dried in vacuo, yielding 800 mg (84%) **10a** as an orange powder.

**Data for 10a:** MS (FAB): $m/z$ = 522 $[M]^+$ was not observed, due to clustering signals of higher masses were detected. $^1H$ NMR (300 MHz, $CD_2Cl_2$): δ = 1.05 [d, $^3J_{H,H}$ = 6.6 Hz, 6 H, $CH(CH_3)_2$], 1.46 (d, $^3J_{H,H}$ = 6.9 Hz, 6 H, $CH(CH_3)_2$], 3.21 [m, 5 H, 2 × $CH(CH_3)_2$, N−$CH_3$], 6.98−7.93 (m, 10 H, $C_6H_5$, $C_6H_3$, $C_3H_2N_2$) ppm. $^{13}C$ NMR (75.432 MHz, $CD_2Cl_2$): δ = 23.3, 24.7, 29.1 [$CH(CH_3)_2$], 37.5 (N−$CH_3$), 123.6, 127.7, 127.9, 128.4, 128.8, 129.5, 129.7, 132.3, 140.3, 140.8, 146.3 ($C_6H_5$, $C_6H_3$, $C_3H_2N_2$), 165.7 (C=N) ppm. $C_{23}H_{27}Cl_2N_3Pd$ (522.81): calcd. C 52.84, H 5.21, N 8.04; found C 52.76, H 5.20, N 8.10. Single-crystal X-ray structure: Table 1, Figure 2.

**Palladium(II) Complex 10b:** A Schlenk tube was charged with **3b** (165 mg, 0.302 mmol), of THF (40 mL) and an excess of potassium hydride (25 mg, 0.62 mmol). $H_2$ evolution commenced immediately and the mixture was stirred for 3 hours at ambient temperature, after that period no more gas evolution was observed. The slightly yellow suspension was filtered under protection from air through a short plug of glass wool to remove excess KH and most of the potassium trifluoromethanesulfonate. $PdCl_2$ (65 mg, 0.363 mmol) was added to the resulting slightly turbid solution and the mixture was stirred at room temperature for 24 hours, resulting in a brown suspension. Workup: the volatiles were removed on a rotary evaporator, the brown residue was chromatographed on alumina with dichloromethane and acetonitrile as eluent, the brown fraction was decolorized with activated charcoal, and the solvents were removed in vacuo, affording 147 mg of **10b** as a yellow solid in 85% yield. IR (KBr): $\tilde{\nu}$ = 2961 (m), 2869 (m), 1588 (m), 1487 (s), 1410 (m), 1385 (m), 1346 (s), 1011 (s), 789 (m), 746 (s), 713 (s) $cm^{-1}$. MS (FAB): $m/z$ = 573 $[M]^+$ was not observed, due to clustering signals of higher masses were detected. $^1H$ and $^{13}C$ NMR spectroscopy were attempted in deuterated acetonitrile, acetone, and dimethyl sulfoxide, respectively, but the solubility of **10b** was insufficient to obtain meaningful NMR spectroscopic data. $C_{27}H_{29}Cl_2N_3Pd$ (572.87): calcd. C 56.61, H 5.10, N 7.33; found C 56.48, H 5.07, N 7.38. Single crystal X-ray structure: Table 1, Figure 3.

**Palladium(II) Complex 10c:** A Schlenk tube was charged with **5c** (710 mg, 2.45 mmol), acetonitrile (30 mL), and $PdCl_2$ (435 mg, 2.45 mmol). The mixture was stirred overnight at ambient temperature to afford an orange solution. Workup: the solution was filtered through celite and chromatographed on silica with dichloromethane and acetonitrile as eluent, the orange fraction was collected, solvents were removed on a rotary evaporator, the product was dried in vacuo, and recrystallized from acetonitrile, yielding 1.03 mg (90%) **10c** as orange crystals. MS (FAB): $m/z$ = 467 $[M]^+$ was not observed, due to clustering signals of higher masses were detected. $^1H$ NMR (300 MHz, $CD_3CN$): δ = 2.22, 2.34 (6 H, 2 × s, $CH_3$), 3.11 (s, 3 H, N−$CH_3$), 6.89−7.47 (m, 10 H, $C_6H_5$, $C_6H_3$, $C_3H_2N_2$) ppm. $^{13}C$ NMR (75.432 MHz, $CD_3CN$): δ = 19.4 ($CH_3$), 37.3 (N−$CH_3$), 127.5, 127.9, 128.2, 128.5, 128.7, 129.8, 130.9, 131.9, 132.5, 144.1, 147.4 ($C_6H_5$, $C_6H_3$, $C_3H_2N_2$), 167.5 (C=N) ppm. $C_{19}H_{19}Cl_2N_3Pd$ (466.71): calcd. C 48.90, H 4.10, N 9.00; found C 49.10, H 4.15, N 8.94. Single crystal X-ray structure: Table 1, Figure 4.

**Palladium(II) Complex 10d:** A Schlenk tube was charged with **5d** (545 mg, 1.62 mmol), acetonitrile (30 mL) and $PdCl_2$ (286 mg, 1.62 mmol). The mixture was stirred overnight at ambient temperature to afford an orange solution. Workup: the solution was filtered through celite and chromatographed on silica with dichlorometh-

ane and acetonitrile as eluent, the orange fraction was collected, solvents were removed on a rotary evaporator, the product was dried in vacuo, and recrystallized from a mixture of dichloromethane and acetonitrile, yielding 835 mg (98%) **10d** as orange crystals. MS (FAB): $m/z$ = 515 $[M]^+$ was not observed, due to clustering signals of higher masses were detected. $^1H$ and $^{13}C$ NMR spectroscopy were attempted, but the solubility of **10d** was insufficient to obtain meaningful NMR spectroscopic data. $C_{23}H_{19}Cl_2N_3Pd$ (514.47): calcd. C 53.67, H 3.72, N 8.16; found C 53.37, H 3.75, N 8.21.

**Nickel(II) Complex 10e:** A Schlenk tube was charged with **5a** (787 mg, 2.28 mmol), acetonitrile (30 mL) and $NiBr_2$ (550 mg, 2.52 mmol). The mixture was stirred overnight, giving a green suspension. Workup: acetonitrile was removed on a vacuum line, the residue was dissolved in dry dichloromethane, the solution was filtered through a Schlenk frit to remove excess $NiBr_2$, and the solution was evaporated to dryness on a vacuum line, affording 1.22 g (95%) **10e** as a green-brown, paramagnetic, air-sensitive powder. $^1H$ NMR in deuterated dimethyl sulfoxide showed only very broad signals. $C_{23}H_{27}Br_2N_3Ni$ (563.98): calcd. C 48.98, H 4.83, N 7.45; found C 48.70, H 4.89, N 7.58.

**Nickel(II) Complex 10f:** A Schlenk tube was charged with **5c** (510 mg, 1.76 mmol), dichloromethane (40 mL) and $NiBr_2$·DME (544 mg, 1.76 mmol). The mixture was stirred for 48 hours at room temperature, giving a brown solution. Workup: dichloromethane was removed on a vacuum line, affording 814 mg (91%) **10f** as a brown, paramagnetic, air-sensitive powder. $^1H$ NMR spectra, in deuterated dimethyl sulfoxide, showed only very broad signals. $C_{19}H_{19}Br_2N_3Ni$ (507.88): calcd. C 44.93, H 3.77, N 8.27; found C 44.54, H 3.67, N 7.96.

**Nickel(II) Complex 10g:** A Schlenk tube was charged with **5d** (480 mg, 1.42 mmol), dichloromethane (40 mL) and $NiBr_2$·DME (439 mg, 1.42 mmol). The mixture was stirred for 48 hours at room temperature, giving a green solution. Workup: dichloromethane was removed on a vacuum line, affording 790 mg (99%) **10g** as a green, paramagnetic, air-sensitive powder. $^1H$ NMR spectra, in deuterated dimethyl sulfoxide, showed only very broad signals. $C_{23}H_{19}Br_2N_3Ni$ (555.92): calcd. C 49.69, H 3.44, N 7.56; found C 49.21, H 3.51, N 7.42.

**X-ray Crystallography:** Single-crystal X-ray measurements and structure determinations of **3b, 10a, 10b, 10c** (Table 1, Figures 1−4): The data collection was performed on a Nonius Kappa CCD equipped with graphite-monochromatized Mo-$K_\alpha$-radiation ($\lambda$ = 0.71073 Å) and a nominal crystal to area detector distance of 36 mm. Intensities were integrated using DENZO and scaled with SCALEPACK.[25] Several scans in the φ and ω directions were made to increase the number of redundant reflections, which were averaged in the refinement cycles. This procedure replaces an empirical absorption correction. The structures were solved with direct methods (SHELXS-86) and refined against $F^2$ (SHELX-97).[26] Hydrogen atoms at carbon atoms were added geometrically and refined using a riding model. All non-hydrogen atoms were refined with anisotropic displacement parameters.

CCDC-216464 (for **3b**), -216465 (for **10a**), -216466 (for **10b**), -216467 (for **10c**) contain the crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

## Acknowledgments

We thank BASF Aktiengesellschaft, Ludwigshafen, Germany for financial support and for preliminary ethene polymerizations as well as for investigations of C−C cross-coupling Suzuki reactions.

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Received January 28, 2004
Early View Article
Published Online May 13, 2004

  